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Palladium imine and amine complexes derived from 2-thiophenecarboxaldehyde as catalysts for the Suzuki cross-coupling of aryl bromides

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Abstract

A range of square-planar *trans*-dichloro palladium(II) complexes containing *N*-(2-thienylmethylene)-aniline and *N*-(2-thienylmethyl)-aniline derived ligands has been synthesized and characterized. The use of these complexes as catalysts for the Suzuki coupling of various aryl bromides and phenyl boronic acid has been examined.

Keywords: 2-Thiophenecarboxaldehyde; Imine ligands; Amine ligands; Suzuki cross-coupling; Palladium complexes

1. Introduction

Palladium-catalyzed Suzuki cross-coupling reactions of aryl halides with arylboronic acids have emerged as an extremely efficient and thus important tool in organic synthesis [1]. Accordingly, in the past few years many efforts have been made to develop new catalytic systems [2–6]. Among the various palladium-catalyzed systems reported, complexes containing sterically demanding chelating α-diimine (diazabutadiene) and β-diimine ligands have been found to be highly efficient as catalysts for Suzuki cross-coupling reactions [7]. In contrast to these types of catalysts, palladium compounds containing monodentate imine ligands have not been utilized as catalysts for Suzuki coupling reactions. Here we wish to report on the synthesis and characterization of a series of palladium complexes containing *N*-(2-thienylmethylene)-aniline and *N*-(2-thienylmethyl)-aniline derived ligands and describe the use of these palladium complexes in the catalytic cross-coupling of various aryl bromides with phenylboronic acid.

2. Experimental

2.1. General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures. The starting materials 2-thiophenecarboxaldehyde and 2,4,6-trimethylaniline were purchased from Aldrich and used without further purification. 1-Propaneamine was purchased from Merck, *S*-(−)-1-phenylethylamine was purchased from Fluka. The ligands *N*-(2-thienylmethylene)-1-propaneamine (**1b**), *S*-(−)-*N*-(2-thienylmethylene)-1-phenylethylamine (**1c**) [8], and *N*-(2-thienylmethyl)-aniline (**2**) were prepared according to the literature [9].

The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker AVANCE-250 spectrometer and were referenced to $SiMe_4$. ^{1}H and $^{13}C\{^{1}H\}$ NMR signal assignments were confirmed by ^{1}H-COSY and 135-DEPT experiments.

2.2. Ligand synthesis

2.2.1. 2,4,6-Trimethyl-N-(2-thienylmethylene)-aniline (*1a*)

This ligand has been prepared according to the procedure reported for imine ligands **1b** and **1c** [8]. A solution of

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2-thiophenecarboxaldehyde (1.25 mL, 13.38 mmol) in 50 mL of ethanol was treated with 2,4,6-trimethylaniline (1.88 mL, 13.38 mmol). The solution was stirred overnight at room temperature. Upon removal of the solvent a yellow solid was obtained which was purified by recrystallisation from petroleum ether and ethyl acetate (1:1). Yield: 2.19 g (71%). Anal. Calcd. for $C_{14}H_{15}NS$: C, 73.32; H, 6.59; N, 6.11. Found: C, 73.12; H, 6.69; N, 6.00. ^{1}H NMR ($CDCl_3$): δ 8.32 (s, 1H, N = CH), 7.54 (d, J = 5.1 Hz, 1H, thiophene), 7.45 (d, J = 3.5 Hz, 1H, thiophene), 7.17 (dd, J = 4.9 Hz, J = 3.8 Hz, 1H, thiophene^4), 6.91 (s, 2H, Ph^{3,5}–H), 2.32 (s, 3H, Ph^4–CH$_3$), 2.18 (s, 6H, Ph^{2,6}–CH$_3$). ^{13}C NMR ($CDCl_3$): δ 155.6 (N=C), 147.9 and 142.6 (thiophene^2 and Ph^1), 133.0 and 127.3 (Ph^{2,6} and Ph^4), 131.6, 129.9, and 127.6 (thiophene^{3,4,5}), 128.6 (Ph^{3,5}), 20.7 (Ph^4–CH$_3$), 18.2 (Ph^{2,6}–CH$_3$).

2.3. Synthesis of palladium complexes

2.3.1. Pd(COD)Cl$_2$

A suspension of $PdCl_2$ (5.00 g, 28.2 mmol) in methanol (150 mL) was treated with 1,5-cyclooctadiene (COD) (10.4 mL, 84.6 mmol) and stirred for 48 h at room temperature. During that time the color of the suspension changed from red to yellow. The yellow solid was collected on a glass-frit, washed with methanol, and dried under vacuum. Yield: 7.29 g (91.0%). Spectral data were identical with those of the authentic sample reported elsewhere [10].

2.3.2. Dichlorobis-κ-N-[2,4,6-trimethyl-N-(2-thienylmethylene)-aniline]palladium(II) (**3a**)

A solution of **1a** (0.40 g, 1.74 mmol) in dry toluene was treated with Pd(COD)Cl$_2$ (0.25 g, 0.87 mmol) and stirred at 70 °C for 16 h. The solvent was removed and the crude product washed three times with diethylether and dried in vacuo. Yield: 0.48 g (87%). Anal. Calcd. for $C_{28}H_{30}Cl_2N_2PdS_2$: C, 52.88; H, 4.75; N, 4.40. Found: C, 53.02; H, 4.65; N, 4.50. ^{1}H NMR ($CDCl_3$): δ 9.09 (d, J = 1.3 Hz, 1H, N = CH), 7.53 (dd, J = 3.8 Hz, J = 1.1 Hz, 1H, thiophene), 7.44 (dt, J = 5.1 Hz, J = 1.2 Hz, 1H, thiophene), 7.00 (dd, J = 5.0 Hz, J = 3.9 Hz, 1H, thiophene^4), 6.94 (s, 2H, Ph^{3,5}–H), 2.32 (s, 6H, Ph^{2,6}–CH$_3$), 2.31 (s, 3H Ph^4–CH$_3$). ^{13}C NMR ($CDCl_3$): δ 165.5 (N=C), 142.4 and 137.7 (thiophene^2 and Ph^1), 139.6, 136.4, and 126.8 (thiophene^{3,4,5}), 134.5 (Ph^4), 131.3 (Ph^{2,6}), 130.3 (Ph^{3,5}), 21.2 (Ph^4–CH$_3$), 19.4 (Ph^{2,6}–CH$_3$).

2.3.3. Dichlorobis-κ-N-[N-(2-thienylmethylene)-1-propaneamine]palladium(II) (**3b**)

This complex has been prepared analogously to **3a** with **1b** (0.30 g, 1.96 mmol) and Pd(COD)Cl$_2$ (0.28 g, 0.98 mmol) as the starting materials. Yield: 0.40 g (85%). Anal. Calcd. for $C_{16}H_{22}Cl_2N_2PdS_2$: C, 39.72; H, 4.58; 5.79. Found: C, 39.81; H, 4.55; 5.58. ^{1}H NMR ($CDCl_3$): δ 8.03 (s, 1H, N = CH), 7.84 (d, J = 5.1 Hz, 1H, thiophene), 7.65 (dd, J = 3.8 Hz, J = 1.0 Hz, 1H, thiophene), 7.22 (dd, J = 4.9 Hz, J = 3.8 Hz, 1H, thiophene^4), 4.00 (t, J = 7.5 Hz, 2H, N–CH$_2$), 2.36–2.21 (m, 2H, CH$_2$–CH$_3$), 1.06 (t, J = 7.3 Hz, 3H, CH$_3$). ^{13}C NMR ($CDCl_3$) δ 161.2 (N=C), 138.5, 134.2, and 127.3 (thiophene^{3,4,5}), 136.3 (thiophene^2), 67.0 (N–CH$_2$), 22.9 (CH$_2$–CH$_3$), 11.6 (CH$_3$).

2.3.4. Dichlorobis-κ-N-[S-(−)-N-(2-thienylmethylene)-1-phenylethylamine]palladium(II) (**3c**)

This complex has been prepared analogously to **3a** with **1c** (0.41 g, 1.90 mmol) and Pd(COD)Cl$_2$ (0.21 g, 0.74 mmol) as the starting materials. Yield: 0.31 g (85%). Anal. Calcd. for $C_{26}H_{26}Cl_2N_2PdS_2$: C, 51.37; H, 4.31; N, 4.61. Found: C, 51.25; H, 4.21; N, 4.57. ^{1}H NMR ($CDCl_3$): δ 7.80 (d, J = 4.9 Hz, 1H, thiophene), 7.75 (s, 1H, N = CH), 7.70-7.65 (m, 2H, thiophene and Ph), 7.45–7.31 (m, 4H, Ph-H), 7.15 (dd, J = 4.9 Hz, J = 3.8 Hz, 1H, thiophene^4), 6.22 (q, J = 6.9 Hz, 1H, N–CH–CH$_3$), 2.12 (d, J = 7.0 Hz, 1H, N–CH–CH$_3$). ^{13}C NMR ($CDCl_3$): δ 162.1 (N=C), 139.4 and 136.8 (thiophene^2 and Ph^1), 138.6, 134.4, and 127.2 (thiophene^{3,4,5}), 128.9, 128.8, and 128.4 (Ph^{2,3,4,5,6}), 69.3 (N–CH–CH$_3$), 19.9 (N–CH–CH$_3$).

2.3.5. Dichlorobis-κ-N-[N-(2-thienylmethyl)-aniline]palladium(II) (**4**)

This complex has been prepared analogously to **3a** with **2** (0.30 g, 1.59 mmol) and Pd(COD)Cl$_2$ (0.09 g, 0.32 mmol) as the starting materials. Yield: 0.13 g (81%). Anal. Calcd. for $C_{22}H_{22}Cl_2N_2PdS_2$: C, 47.53; H, 3.99; N, 5.04. Found: C, 47.77; H, 4.12; N, 4.89. ^{1}H NMR ($CDCl_3$): δ 7.43–7.25 (m, 5H, thiophene-H and Ph-H), 7.21–7.15, 7.04–6.99, and 6.88–6.81 (m, 3H, thiophene-H and Ph-H), 5.27 (d, J = 6.3 Hz, 1H, NH), 4.94–4.78 (m, 1H, N–CH$_2$), 4.26–4.18 (m, 1H, N–CH$_2$). ^{13}C NMR ($CDCl_3$): δ 143.8 (Ph^1), 135.9 (thiophene^2), 129.5 (Ph^{3,5}), 129.1, 126.8, 126.7, and 126.6 (thiophene^{3,4,5}and Ph^4), 122.0 and 121.9 (Ph^2 and Ph^6), 51.7 (N–CH$_2$).

2.4. General procedure for the palladium-catalyzed Suzuki cross-coupling

The substrate (1.00 mmol), phenyl boronic acid (1.5 mmol), and 2.00 mmol of Cs_2CO_3 were suspended in 5 mL of dry 1,4-dioxane, charged with the respective amount of catalyst, and stirred at 110 °C for 18 h. After that, the mixture was cooled to room temperature and diluted with 10 mL of a 2N aqueous NaOH solution. The aqueous phase was extracted three times with dichloromethane, dried over Na_2SO_4, and evaporated to dryness. The crude product was purified via column chromatography over silica gel (petroleum ether:ethyl acetate (20:1)).

2.5. X-ray structure determination

X-ray data for **3a** $ClCH_2CH_2Cl$, **3b** $ClCH_2CH_2Cl$, and **4** were collected on a Bruker Smart CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space. Corrections for absorption, λ/2 effects, and crystal decay were applied [11]. The structures were solved by direct methods using the program SHELXS97 [12] structure refinement on F^2 was carried out with the program SHELXL97 [12]. All non-hydrogen atoms were refined

Table 1
Details for the crystal structure determinations of complexes **3a** $ClCH_2CH_2Cl$, **3b** $ClCH_2CH_2Cl$, and **4**

	3a $ClCH_2CH_2Cl$	**3b** $ClCH_2CH_2Cl$	**4**
Formula	$C_{30}H_{34}Cl_4N_2PdS_2$	$C_{18}H_{26}Cl_4N_2PdS_2$	$C_{22}H_{22}Cl_2N_2PdS_2$
fw	734.91	582.73	555.84
Crystal size (mm)	0.63 × 0.38 × 0.17	0.29 × 0.24 × 0.197	0.25 × 0.22 × 0.18
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*C*2/*c* (number 15)	$P2_1/c$ (number 14)	$P2_1/n$ (number 14)
a (Å)	14.0954(6)	8.8537(3)	6.4398(7)
b (Å)	10.3528(4)	13.4687(5)	7.8355(8)
c (Å)	21.8652(9)	10.9671(4)	21.922(2)
β (°)	98.874(1)	111.226(1)	91.983(2)
V (Å^3)	3152.5(2)	1219.08(8)	1105.5(2)
Z	4	2	2
ρ_{calc} (g cm^{-3})	1.548	1.587	1.670
T (K)	173(2)	223(2)	100(2)
μ (mm^{-1}) (Mo Kα)	1.084	1.378	1.282
F(0 0 0)	1496	588	560
θ_{max} (°)	30	30	30
Number of rflns measured	28633	13449	8641
Number of unique rflns	4577	3537	3192
Number of rflns $I > 2\sigma(I)$	4342	3206	2994
Number of params	191	122	133
R_1 ($I > 2\sigma(I)$)[a]	0.0261	0.0225	0.0411
R_1 (all data)	0.0276	0.0250	0.0448
wR_1 (all data)	0.0683	0.0587	0.0820
Difference of four peaks min/max (eÅ^{-3})	−0.85/0.67	−0.62/0.87	−0.59/0.66

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum(w(F_o^2 - F_c^2)^2) / \sum(w(F_o^2)^2)]^{1/2}$.

anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. Salient crystallographic data are given in Table 1. Views of the Pd complexes, all being centrosymmetric at Pd, are shown in Figs. 1–3 (primed atoms are inversion related to unprimed atoms). CCDC 273494, 297222, and 297223 contain the supplementary crystallographic data for this paper. These data can

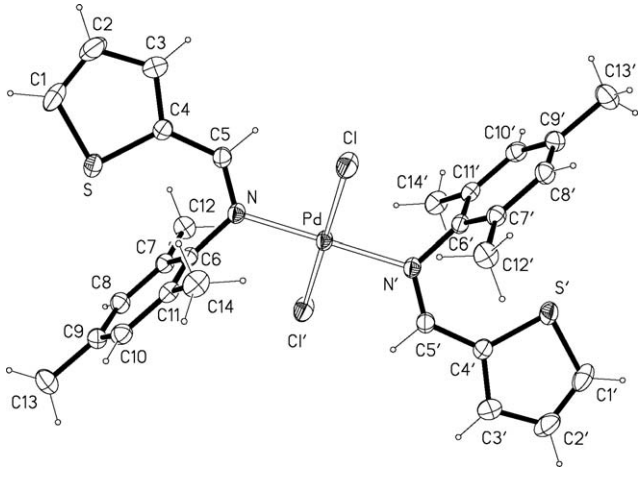


Fig. 1. Structural view of dichlorobis-κ-*N*-[2,4,6-trimethyl-*N*-(2-thienylmethylene)-aniline]palladium(II) $ClCH_2CH_2Cl$ (**3a** $ClCH_2CH_2Cl$) showing 50% thermal ellipsoids (dichloroethane omitted for clarity). Selected bond lengths (Å) and bond angles (°): Pd—N=Pd—N' 2.054(2); Pd—Cl=Pd—Cl′ 2.3010(4); N—C(5) 1.289(2); N—C(6) 1.442(2); Cl—Pd—Cl′ = N—Pd—N′ 180.0; Cl—Pd—N 89.16(4).

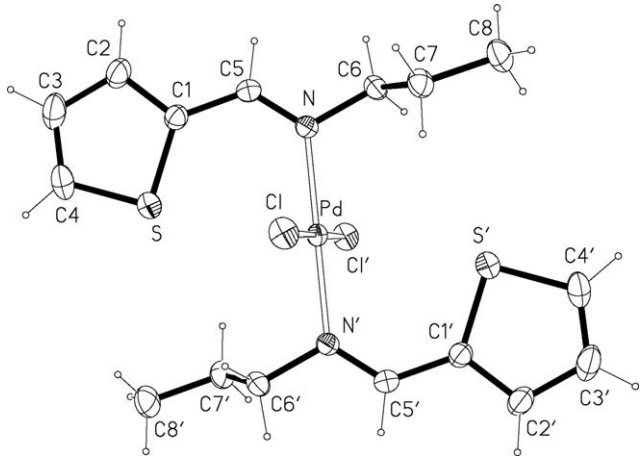


Fig. 2. Structural view of dichlorobis-κ-*N*-[*N*-(2-thienylmethylene)-1-propaneamine] palladium(II) $ClCH_2CH_2Cl$ (**3b** $ClCH_2CH_2Cl$) showing 30% thermal ellipsoids (dichloroethane omitted for clarity). Selected bond lengths (Å) and bond angles (°): Pd—N=Pd—N′ 2.018(1); Pd—Cl=Pd—Cl′ 2.3043(4); N—C(5) 1.276(2); N—C(6) 1.473(2); Cl—Pd—Cl′=N—Pd—N′ 180.0; Cl—Pd—N′ 89.51(4).

be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

Treatment of $Pd(COD)Cl_2$ with ligands **1a**–**1c** and **2** in toluene for 16 h afforded complexes **3a**–**3c** and **4** cleanly in high

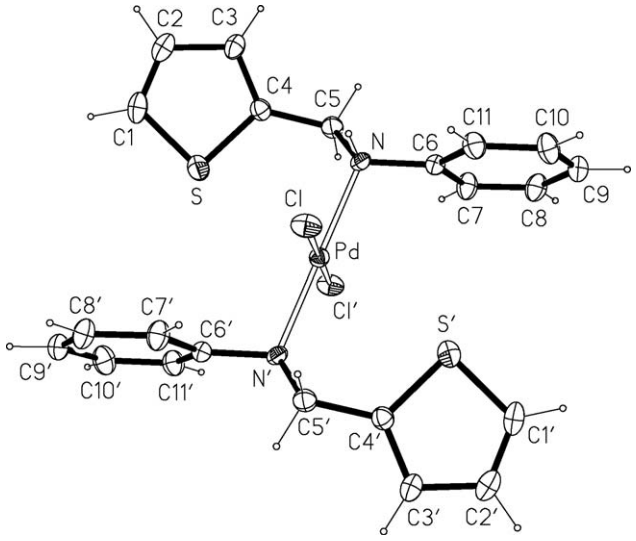


Fig. 3. Structural view of dichlorobis-κ-*N*-[*N*-(2-thienylmethyl)-aniline]-palladium(II) (**4**) showing 50% thermal ellipsoids. Selected bond lengths (Å) and bond angles (°): Pd—N=Pd—N′ 2.054(2); Pd—Cl=Pd—Cl′ 2.3090(7); N—C(5) 1.455(3); N—C(6) 1.499(3); Cl—Pd—Cl′=N—Pd—N′ 180.0; Cl—Pd—N 86.38(7).

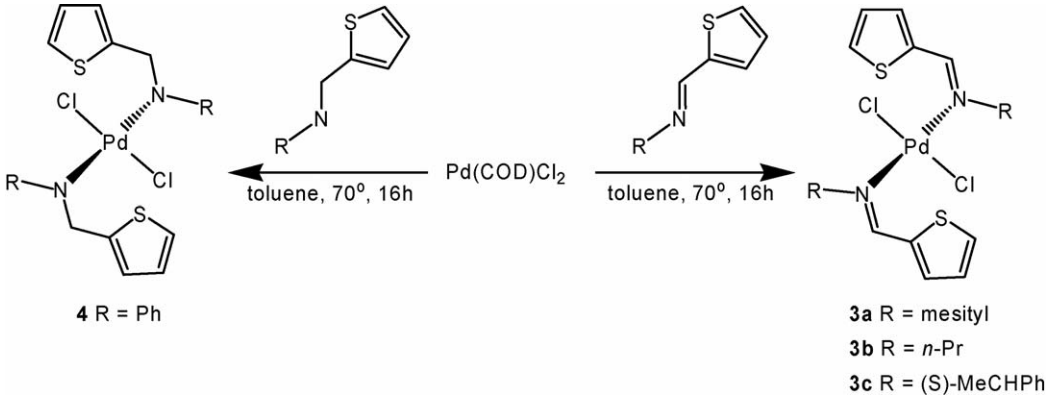
isolated yields (Scheme 1). The synthesis of related dichlorobis-κ-*N*-[*N*-(2-thienylmethylene)-aniline]palladium(II) complexes has been published recently [13]. It has to be noted that the synthesis of **3b** has been described elsewhere but no spectroscopical or X-ray data have been presented [14]. All complexes are thermally robust yellow solids which are stable to air both in the solid state and in solution. The identity of the compounds was established by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy, and by elemental analysis.

From the NMR spectroscopical data it is obvious that the thienyl moiety is still intact and orthopalladation to form a chelating κ^2-C,N bound imine ligand, as has been frequently observed in related systems, did not occur. The NMR spectra of **3a**–**3c** and **4** bear no unusual features and it is sufficient to point out that the proton of the imine CH=N moiety of the imine ligands gives a characteristic singlet resonance in the range of 7.75–9.09 ppm. Likewise, in the $^{13}C\{^{1}H\}$ NMR spectra the imine carbon atoms exhibit a singlet resonance between 161 and 165 ppm. Structural views of **3a**, **4b**, and **4**, as determined by X-ray crystallography, are depicted in Figs. 1–3. Selected geometric data are reported in the captions. The complexes are in their *trans* form and the coordinated imine and amine ligands, respectively, are coordinated via the nitrogen atoms in monodentate fashion. The molecules display the usual square-planar coordination around the palladium center. All Pd–N and Pd–Cl bond lengths lie within the expected range for *trans*-N–Pd–N and Cl–Pd–Cl arrangements [13].

Palladium complexes containing α- and β-diimine ligands are excellent catalysts for the Suzuki coupling [7]. Based on these findings we were interested in whether palladium complexes containing monodentate imine as well as amine ligands exhibit similar reactivities in C–C bond coupling reactions. Accordingly, we investigated the activity of **3a**–**3c** and **4** for the coupling of various aryl bromides with phenyl boronic acid. The results of this study are summarized in Table 2. In most cases the reactions were performed with 1 mol% of catalysts in dioxane at 110 °C with 2 equivs of Cs_2CO_3 acting as base. These conditions have not been optimized.

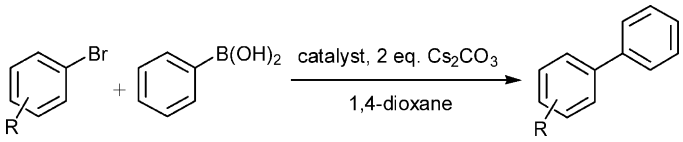
The coupling reaction of 4-bromoanisole with phenyl boronic acid catalyzed by **3a**–**3c** and **4** and a catalyst loading of 1 mol% afforded 4-methoxybiphenyl in 96, 29, 16, and 35% isolated yields (entries 1, 4–6). Even with 0.01 mol% of **3a** 20% of 4-methoxybiphenyl are obtained (entry 3). The coupling of the electronically activated substrate 4-bromoacetophenone with phenyl boronic acid proceeds with all catalysts resulting in yields >93% (entries 7–11). Attempts to couple 4-chloroacetophenone with phenyl boronic acid resulted in almost no conversion (entry 20). While it is difficult to establish a clear trend in the catalytic activity of complexes **3a**–**3c** and **4** on these preliminary data, on average, complex **3a** shows higher activity than the other complexes. This is especially apparent in the coupling of the electronically deactivated and thus more challenging substrate 4-bromoanisole with phenyl boronic acid. This reactivity trend may suggest that the bulkier mesityl substituent renders the catalyst more active. Finally, the catalytic effect was confirmed by running the standard reaction on 4-bromoacetophenone and 4-bromoanisole with $PdCl_2$. The reaction proceeds, but led to much lower yields.

It has to be noted that recently evidence was presented that pincer ligands are merely pre-catalysts generating some forms



Scheme 1.

Table 2
Yields of the Suzuki cross-coupling of aryl bromides with phenyl boronic acid catalyzed by **3a**–**3c**, and **4**[a]



Entry	Substrate	Catalyst (mol%)	Yield (%)
1	4-Bromoanisole	**3a** (1)	96
2	4-Bromoanisole	**3a** (0.1)	68
3	4-Bromoanisole	**3a** (0.01)	20
4	4-Bromoanisole	**3b** (1)	29
5	4-Bromoanisole	**3c** (1)	16
6	4-Bromoanisole	**4** (1)	35
7	4-Bromoacetophenone	**3a** (0.01)	>99
8	4-Bromoacetophenone	**3a** (0.001)	4
9	4-Bromoacetophenone	**3b** (1)	>99
10	4-Bromoacetophenone	**3c** (1)	93
11	4-Bromoacetophenone	**4** (1)	>99
12	1-Bromo-4-nitrobenzene	**3a** (0.1)	97
13	1-Bromo-4-nitrobenzene	**3a** (0.01)	0
14	1-Bromo-4-nitrobenzene	**3b** (1)	95
15	1-Bromo-4-nitrobenzene	**3c** (1)	94
16	2-Bromopyridine	**3a** (1)	77
17	2-Bromopyridine	**3b** (1)	61
18	Bromobenzene	**3a** (1)	31[b]
19	Bromobenzene	**3a** (1)	87
20	4-Chloroacetophenone	**3a** (1)	5

[a] Reaction conditions: 1.0 mmol bromide; 1.5 mmol $PhB(OH)_2$; 2.0 mmol Cs_2CO_3; 5 mL dioxane, 110 °C; reaction time is 18 h, yields represent isolated yields (average of at least two experiments) of compounds estimated to be ≥95% pure as judged by ^1H NMR.
[b] The reaction was stirred at 90 °C.

of metallic palladium(0) which actually does the catalysis [15]. Pincer ligands possessing only phosphinito donors decomposed even more easily and lead to more active sources of metallic palladium. In the present catalytic reactions we cannot exclude such a possibility since in some cases the formation of palladium black was observed.

4. Conclusion

We have successfully prepared new palladium(II) complexes containing *N*-(2-thienylmethylene)-aniline and *N*-(2-thienylmethyl)-aniline derived ligands. These complexes were found to be active as catalysts for Suzuki coupling reactions and are comparable to related α- and β-dimine systems, thus representing an interesting alternative to existing catalytic systems. Qualitatively, it was found that complexes with imine ligands featuring sterically demanding substituents such as mesityl are clearly better catalysts.

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